(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: 0 522 651 A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 92202060.7

(51) Int. Cl.5: C08F 4/656, C08F 10/02

(22) Date of filing: 07.07.92

(30) Priority: 12.07.91 IT MI911938

(43) Date of publication of application:
13.01.93 Bulletin 93/02

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU MC NL PT SE

(71) Applicant: E C P ENICHEM POLIMERI S.r.L.
Piazza della Repubblica 16
I-20121 Milan(IT)

(72) Inventor: Luciani, Luciano
Via Mac Alister 37
I-44100 Ferrara(IT)
Inventor: Milani, Federico
Via Kennedy 2
I-45030 Santa Maria Maddalena Rovigo(IT)
Inventor: Invernizzi, Renzo
Via Primaticcio 98
I-20147 Milan(IT)
Inventor: Pondrelli, Maddalena
Via Gramsci 54
I-40054 Budrio Bologna(IT)

(74) Representative: Roggero, Sergio et al
Ing. Barzanò & Zanardo Milano S.p.A. Via Borgonuovo 10
I-20121 Milano(IT)

(54) Supported catalyst for the (CO)polymerization of ethylene.

(57) A solid component of catalyst for the (co)polymerization of ethylene is composed of a silica support and of a catalytically active part containing titanium, magnesium, chlorine and alkoxy groups, and is obtained by;

(i) activating a silica support by contact with a solution of magnesium dialkyl, or magnesium alkyl chloride, in a liquid, aliphatic hydrocarbon solvent;

(ii) impregnating the activated silica with a solution, in a liquid aliphatic or aromatic ester, of titanium tetrachloride and tetra-alkoxide in equimolecular or almost equimolecular quantities, and magnesium chloride; and

(iii) treating the solid obtained in step (ii) with a proportioned quantity of aluminium alkyl sesquichloride.

EP 0 522 651 A2

3NSDOCID: <EP___0522651A2_I_>

examples a microspheroidal silica is used as the support of the solid component in catalyst, in particles with an average diameter of 40 μm and having the following characteristics:

- apparent density:	0.21 g/ml
- surface area (BET):	320 m^2/g
- pore volume:	1.6 ml/g
- average pore diameter:	25 A

EXAMPLE 1

(i) 20 ml (17.5 mmoles) of 20% by weight $Mg(C_4H_9)_{1.5}(C_8H_{17})_{0.5}$ in n-heptane and 17 g of silica are charged, in a nitrogen atmosphere, into a 500 ml flask, equipped with a reflux cooler, mechanical stirrer and thermometer. The mixture is heated to 60°C for 1 hour under stirring and the activated silica is then recovered by filtration.

(ii) 220 ml ethyl acetate, 4.96 g (14.6 mmoles) of titanium tetra n-butoxide, 1.6 ml (14.5 mmoles) of titanium tetrachloride and 2.79 g (29.4 mmoles) of magnesium chloride are charged, in a nitrogen atmosphere, into another 500 ml flask, equipped with a reflux cooler, mechanical stirrer and thermometer. The mixture is heated to reflux temperature (about 75°C) for 1 hour until the magnesium chloride has completely dissolved. The activated silica is then added to the solution thus obtained as described in (i). Contact is left for 1 hour at 70°C and the solution is then dried by evaporating the solvent.

(iii) The impregnated silica thus obtained is suspended in 300 ml of n-hexane and 8.81 g (35.6 mmoles) of aluminium ethyl sesquichloride are added to the suspension, at a temperature of 25°C. The temperature is brought to 66°C and the suspension is left to react for 1 hour.

(iv) At the end of this period the solid is recovered from the suspension, washed with anhydrous n-hexane until the chlorides have disappeared from the washing liquid, and finally dried.

28 g of a solid component of catalyst are obtained in the form of a microspheroidal solid, containing 4.3% by weight of titanium (19% of which is in the form of trivalent titanium), 3.8% by weight of magnesium, 18.4% by weight of chlorine and 2.2% by weight of aluminium.

EXAMPLE 2

Example 1 is repeated with the difference that in step (iii) 1.40 g of aluminium ethyl sesquichloride are used.

28.4 g of a component of catalyst are thus obtained in the form of a microspheroidal solid, containing 4.25% by weight of titanium (12% of which is in the form of trivalent titanium), 3.9% by weight of magnesium, 17% by weight of chlorine and 1.8% by weight of aluminium.

EXAMPLE 3

Example 1 is repeated with the difference that in step (iii) 13.2 g of aluminium ethyl sesquichloride are used.

28.0 g of a component of catalyst are thus obtained in the form of a microspheroidal solid, containing 4.3% by weight of titanium (38% of which is in the form of trivalent titanium), 3.4% by weight of magnesium, 19.3% by weight of chlorine and 3.5% by weight of aluminium.

EXAMPLE 4 (comparative)

Example 1 is repeated with the difference that in step (ii) 9.92 g (29.1 mmoles) of titanium tetra n-butoxide are used and titanium tetrachloride is not added.

28.5 g of a component of catalyst are thus obtained in the form of a microspheroidal solid, containing 3.7% by weight of titanium (43% of which is in the form of trivalent titanium), 3.8% by weight of magnesium, 12.4% by weight of chlorine and 1.7% by weight of aluminium.

EXAMPLE 5 (comparative)

Example 1 is repeated with the difference that in step (ii) 9.92 g (29.1 mmoles) of titanium tetra n-

EPOCID <EP 0522651A2 I >

butoxide are used and titanium tetrachloride is not added and in step (iii) 17.6 g (71.2 mmoles) of aluminium ethyl sesquichloride are used.

26.6 g of a component of catalyst are thus obtained in a microspheroidal form, containing 4.4% by weight of titanium (51% of which is in the form of trivalent titanium), 3.7% by weight of magnesium, 19.7% by weight of chlorine and 3.2% by weight of aluminium.

EXAMPLE 6 (comparative)

Example 1 is repeated with the difference that in step (ii) 5.50 g (29.0 mmoles) of titanium tetrachloride are used and titanium tetra n-butoxide is not added and in step (iii) 3.03 g (12.3 mmoles) of aluminium ethyl sesquichloride are used.

28.2 g of a component of catalyst are thus obtained in the form of a microspheroidal solid, containing 4.2% by weight of titanium (24% of which is in the form of trivalent titanium), 3.5% by weight of magnesium, 17% by weight of chlorine and 2.1% by weight of aluminium.

EXAMPLE 7 (comparative)

Example 1 is repeated with the difference that in step (ii) 5.50 g (29.0 mmoles) of titanium tetrachloride are used and titanium tetra n-butoxide is not added and in step (iii) the treatment with aluminium ethyl sesquichloride is omitted.

23.3 g of a component of catalyst are thus obtained in the form of a microspheroidal solid, containing 4.4% by weight of titanium (100% in tetravalent form), 3.8% by weight of magnesium and 13.7% by weight of chlorine.

EXAMPLE 8 (comparative)

Example 1 is repeated with the difference that in step (ii) 5.50 g (29.0 mmoles) of titanium tetrachloride are used and titanium tetra n-butoxide is not added and in step (iii) 6.03 g of aluminium ethyl sesquichloride are used.

24 g of a component of catalyst are thus obtained in the form of a microspheroidal solid, containing 4.1% by weight of titanium (35% of which is in the form of trivalent titanium), 3.6% by weight of magnesium, 19.4% by weight of chlorine and 2.4% by weight of aluminium.

EXAMPLE 9

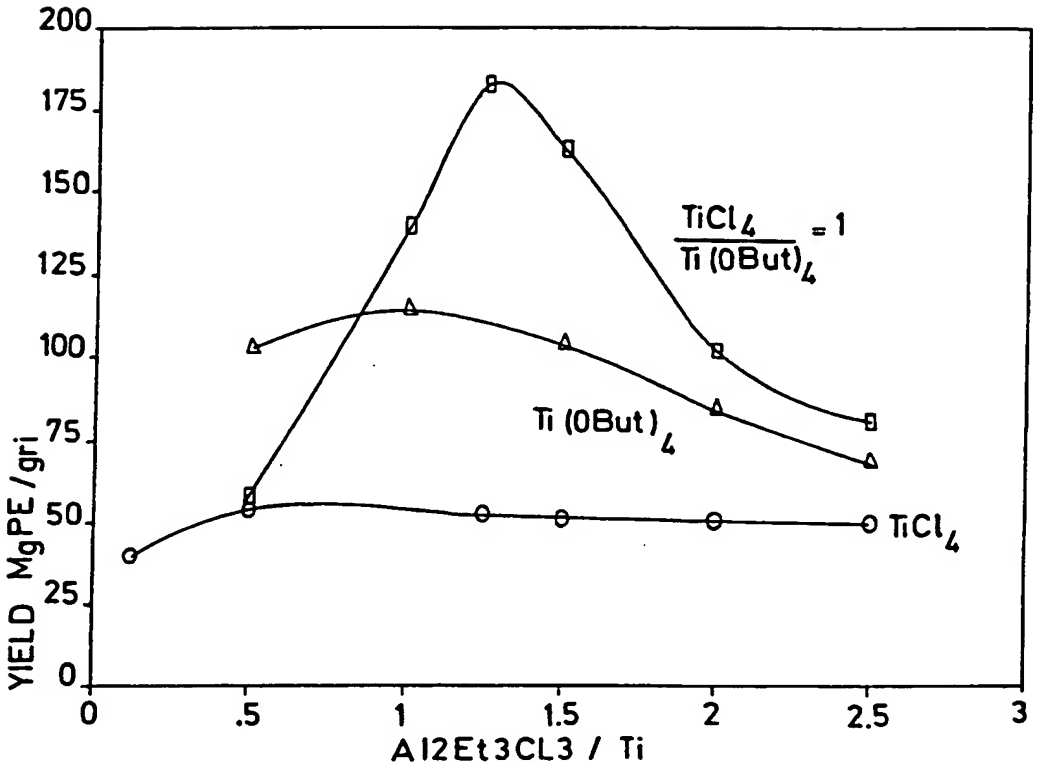
The solid components of catalyst prepared in Examples 1-8 (tests 1-8) are used in polymerization tests of ethylene. More specifically, the polymerization is carried out in an autoclave having a volume of 5 litres containing 2 litres of n-hexane. The operating pressure is 15 bar in the presence of hydrogen, with a ratio between the hydrogen and ethylene pressure of 0.47/1, or 0.64/1, at a temperature of 90 °C and with a time of 1.5 hours, using aluminium triethyl as a co-catalyst, with a molar ratio between the aluminium triethyl and the titanium in the solid component of 50/1. Tests 9-11 are carried out with the solid component of catalyst of Example 1, but using a polymerization time of 3 hours.

Table 1 below shows, for each test, the ratio (RP) between the hydrogen pressure and the ethylene pressure; the yield (Yield) in polyethylene expressed in kg of polyethylene per g of solid component of catalyst; the yield with respect to the titanium (R/Ti) expressed in kg of polyethylene per gram of titanium in the solid component of catalyst; the density (D) of the polymer (ASTM D 1505) expressed in g/ml; the melt-flow index (MFI) of the polymer (ASTM D 1238; 2.16 kg and 21.6 kg) expressed in g/10 minutes; and the apparent density (AD) of the polymer (ASTM D 1895) expressed in g/ml.

Table 2 shows the particle size distribution expressed in μm, in % by weight of the polyethylenes obtained in the polymerization tests indicated in Table 1.

ISDOCID: <EP 0522651A2_I_>

Fig.1


200
175
150
125
100
75
50
25
0
YIELD MgPE/gri
0
.5
1
1.5
2
2.5
3
AI2Et3CL3 / Ti
TiCl4 / Ti(OBut)4 = 1
Ti(OBut)4
TiCl4

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 522 651 A3**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 92202060.7

(51) Int. Cl.[5]: C08F 4/656, C08F 10/02

(22) Date of filing: 07.07.92

(30) Priority: 12.07.91 IT MI911938

(43) Date of publication of application:
13.01.93 Bulletin 93/02

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU MC NL PT SE

(88) Date of deferred publication of the search report:
03.03.93 Bulletin 93/09

(71) Applicant: E C P ENICHEM POLIMERI S.r.L.
Piazza della Repubblica 16
I-20121 Milan(IT)

(72) Inventor: Luciani, Luciano
Via Mac Alister 37
I-44100 Ferrara(IT)
Inventor: Milani, Federico
Via Kennedy 2
I-45030 Santa Maria Maddalena Rovigo(IT)
Inventor: Invernizzi, Renzo
Via Primaticcio 98
I-20147 Milan(IT)
Inventor: Pondrelli, Maddalena
Via Gramsci 54
I-40054 Budrio Bologna(IT)

(74) Representative: Roggero, Sergio et al
Ing. Barzanò & Zanardo Milano S.p.A. Via Borgonuovo 10
I-20121 Milano (IT)

(54) Supported catalyst for the (CO)polymerization of ethylene.

(57) A solid component of catalyst for the (co)-polymerization of ethylene is composed of a silica support and of a catalytically active part containing titanium, magnesium, chlorine and alkoxy groups, and is obtained by:

(i) activating a silica support by contact with a solution of magnesium dialkyl, or magnesium alkyl chloride, in a liquid, aliphatic hydrocarbon solvent;

(ii) impregnating the activated silica with a solution, in a liquid aliphatic or aromatic ester, of titanium tetrachloride and tetra-alkoxide in equimolecular or almost equimolecular quantities, and magnesium chloride; and

(iii) treating the solid obtained in step (ii) with a proportioned quantity of aluminium alkyl sesquichloride.

EP 0 522 651 A3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 92 20 2060

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 463 672 (MONTEDIPE) * example 6 *	1-3,5, 10-11	C08F4/656 C08F10/02
P,Y	* page 1 - page 3 *	1-11	
P,Y	EP-A-0 480 435 (ECP ENICHEM POLIMERI) * the whole document * & IT-A-21 711	1-11	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C08F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 DECEMBER 1992	FISCHER B.R.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)

SDOCID: <EP___0522651A3_I_>